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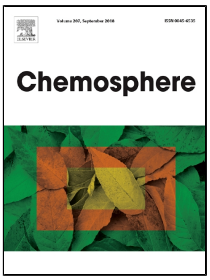

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Jorge F.M. Velez, Yvonne Shashoua, Kristian Syberg, Farhan R. Khan

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Considerations on the use of equilibrium models for the characterisation of HOC-microplastic interactions in vector studies

Jorge F. M. Velez[a], Yvonne Shashoua[b], Kristian Syberg[a], Farhan R. Khan[a]*

[a]Department of Science and Environment, Roskilde University, Universitetsvej 1, PO Box 260, DK-4000 Roskilde, Denmark

[b]Environmental Archaeology and Materials Science, National Museum of Denmark, IC Modewegsvej Brede, DK- 2800, Kongens Lyngby, Denmark

*Corresponding author: frkhan@ruc.dk; farhan.khan@gmx.com (F. R. Khan).

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Abstract

The association of hydrophobic organic contaminants (HOCs) to microplastics (MPs) in the aquatic environment and the possible perturbation of how biota and HOCs interact (i.e. 'MP vector effect') is a much researched topic in the emergent field of aquatic MP pollution. Consensus on whether the vector-effect is relevant can in part be ascertained using laboratory experimentation. Such studies, of which there are now many examples, have as a mandatory component a characterization of the HOC-MP interaction. However, important considerations must be made when planning and executing such laboratory experiments, and subsequently when choosing equilibria models to fit sorption curves, as it is necessary to recognize that simplified conceptual models (i.e. Freundlich or Langmuir models) do not fit all HOC-MP interactions under all circumstances. The sorption equilibrium of HOCs to most plastic particles occurs as a combination of surface adsorption in the crystalline regions of the polymer (typically characterized by Langmuir models) and internal partition into amorphous regions (modelled with Freundlich relations), but this is rarely recognized. In this discussion we highlight some considerations needed when both characterizing the interactions between MPs and HOCs and improving the environmental realism of vector studies through the use of, for instance, weathered particles, adequate time for HOC-MP equilibria to be reached and working at lower concentrations. Increasing environmental realism of vector studies corresponds to a greater complexity in the equilibria model, but ultimately allows better understanding of any potential HOC-MP vector effect in nature.

1. Introduction

Microplastics (MPs <5 mm) are a ubiquitous aquatic pollutant found in marine (Derraik et al., 2002; Ivar do Sol and Costa., 2013) and freshwater habitats (Wagner et al., 2014), and in all compartments of the aquatic environment (water (Eriksen et al., 2013; Desforges et al., 2014), sediment (Claessens et al., 2011; Naji et al., 2017) and biota (Lusher et al., 2013; Biginagwa et al., 2016)). Environmentally sampled MPs have been found with associated concentrations of hydrophobic organic contaminants (HOCs), such as PCBs (polychlorinated biphenyls) and PAHs (polycyclic aromatic hydrocarbons) (Ogata et al., 2009; Rios et al., 2010), as well as other well known pollutants, such as trace metals (Ashton et al., 2010, Holmes et al., 2012, Wang et al., 2017). These studies have raised the possibility that MPs may act as 'vectors' capable of altering the environmental distribution of the adhered pollutants by transporting them, as well as changing their interactions with biota, both at the organismal and cellular levels (Syberg et al., 2015).

Particularly at the organismal level, there has been much laboratory-based research conducted on whether the presence of MPs or the adhesion of exogenous chemicals to MPs influence the uptake and cytotoxicity of said chemicals. Such work has been conducted with trace metals (Khan et al., 2015; Luís et al., 2015) and pharmaceuticals (Syberg et al., 2018), but the vast majority of vector studies combine MPs with HOCs (Oliveria et al., 2013; Chua et al., 2014; Rochman et al., 2013; Besseling et al., 2013; Avio et al., 2015; Paul-Pont et al., 2016) which is the focus of this present discussion. While consensus on the vector impact remains elusive with some studies reporting that MPs have the potential to alter contaminant-organism interactions (Oliveria et al., 2013; Rochman et al., 2013) and others demonstrating minimal impact or reductive effects of MPs (Besseling et al., 2013; Chua et al., 2014), what

has become mandatory in such studies is the need to characterize the sorption processes between HOCs and MPs. However, important considerations must be made when planning and executing laboratory experiments, and subsequently when choosing equilibria models to that fit the results and describe the absorption of pollutants from aqueous solution. It is necessary to recognize that simplified conceptual models, typically Freundlich or Langmuir models, do not fit all HOC-MP interactions under all circumstances. The present discussion aims to highlight considerations needed when characterizing the interactions between MPs and HOCs, which models are most suited for understanding and extrapolating sorption phenomena, and ultimately whether laboratory studies can be sufficiently extrapolated to aid understanding of any potential MP vector effect in nature.

2. Sorption and polymer structure

The polymeric component that often comprises more than 99% of commercial plastic materials consists of a combination of highly ordered crystalline regions and less structured amorphous regions. Whilst the degree of crystallinity can vary greatly, from approximately 50% (e.g. polypropylene and nylon), to almost 0% (e.g. atactic polystyrene), no polymer is 100% crystalline (Fried, 2008). The extent of crystallinity controls the hardness, density, transparency and diffusion properties of polymers. As crystalline areas comprise closely packed polymer chains, they are largely impermeable to gases, liquids and solutions, particularly under ambient conditions. As a result, the rate of migration of materials into plastics and their concentrations at equilibrium are dependent on the percentage of the more loosely packed, amorphous regions (McKeen, 2012). This difference in polymer matrix structure and chain packing is a very important parameter in how HOCs sorb to MPs. Here, ‘sorption’ is used as the generic term for HOC-MP associations, ‘adsorption’ is the surface interaction between HOCs and MPs, and ‘partition’ denotes the diffusion of HOCs into the

MP's internal amorphous regions. Thus, both sorption phenomena can occur simultaneously with all plastic types, while the dominant interaction type at a given concentration is determined by the degree of crystallinity of the polymer present in the MP (Figure 1).

2.1. Partition in amorphous plastics

In highly amorphous polymers most polymer chains are more loosely packed and HOCs can readily diffuse into the spaces between them. Thus, in the aquatic environment, the rate and extent of the sorption of HOCs to predominantly amorphous polymers is dominated by the partition between the water phase and the polymer phase. This interaction, if in equilibrium, is most appropriately modelled by Freundlich equations which describe the sorbed HOCs as a function of aqueous concentration and a constant distribution coefficient (Teuten 2009). Equation 1 illustrates the general Freundlich function where q represents the amount of sorbed solute per unit of sorbent mass, K_d is the Freundlich distribution coefficient and Caq is the solute (or sorbate) concentration in the aqueous phase. To incorporate potential HOC-HOC interactions that may occur as HOC concentrations withn the polymer increase, an empirically determined exponent n ($0 < n < 1$) can be included in the equation:

$$q = K_d C_{aq}^{n} \quad \text{[Eq1]}$$

This empirically-derived equation resembles a two-phase partition equation and can be determined by measuring sorbed HOC concentrations against aqueous HOC concentrations in equilibrium at constant temperature. From this, the Freundlich distribution coefficient is determined from the plotted data (Freundlich isotherms) by regression. It is important to note that Freundlich isotherms do not describe the rates of diffusion into MPs, but assume that equilibrium is reached, regardless of kinetics. The distribution coefficient is strongly dependent on the polar/nonpolar affinity between the HOCs and the polymer into which it

120 partitions, which means that any changes in the polymer's polarity (e.g. introducing polar
121 groups via e.g. photooxidation) or that of the surrounding water (e.g. addition of dissolved
122 organic carbon (DOC) or changes in ionic strength) will influence the solubility of the sorbate
123 in the MP and change the K_d accordingly (O'Connor et al. 2016, Teuten et al. 2009). The
124 assumption that partition solely describes sorption has important implications, chiefly that
125 isotherms determined at high concentrations can be extrapolated to environmentally relevant
126 concentrations.
127
128 **2.2. Adsorption on highly crystalline plastics**
129 Within crystalline regions of plastics, polymer chains are closely packed in a rigid lattice.
130 Lower diffusion coefficients due to this tighter lattice result in surface adsorption rather than
131 internal partition being the dominant sorption process, at least until saturation of surface sites
132 is reached (O'Connor et al. 2016). Adsorption isotherms are always non-linear and level off
133 at the concentration where the surface binding capacity has been reached, which is influenced
134 by the shape and size of the MP. Thus, linear Freundlich models are inadequate in
135 characterizing HOC-MP interactions with highly crystalline plastics. A number of alternative
136 approaches exist. Foo & Hameed (2010) describe thirteen relevant adsorption isotherm
137 models in their review based on different thermodynamic assumptions. However, the
138 simplest and most commonly used non-linear model is the Langmuir model. Langmuir
139 isotherms are derived analytically assuming a reversible adsorption reaction on a single layer
140 with a finite homogeneous area, where there is no interaction between the sorbate's
141 molecules. Adsorption and desorption rates are assumed to be equal (i.e. at equilibrium) and
142 intermolecular interactions are thought to disappear rapidly with distance from the sorbent's
143 surface, so that HOC molecules can only be found in solution or adhered to the MP surface.
144 Equation 2 shows the assumed adsorption reaction and the mathematical expression for the

Langmuir isotherm; where q_e is the mass concentration of the HOC adsorbed to the MP at equilibrium, Q_0 is the maximum possible mass concentration of the HOC adsorbed to the MP at equilibrium, C_e is the concentration of the HOC in the water, and b is related to the strength of binding and the slope of the isotherm at low concentrations. (Xia & Ball 1999, Foo & Hameed 2010).

Reversible adsorption: $HOC + MP \rightleftharpoons HOCMP$

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad \text{[Eq. 2]}$$

Despite the relative simplicity of the Langmuir model, two very important parameters must be kept in mind when performing model experiments; the total amount of surface area per unit of mass or volume of plastic (which depends on particle size, shape, and degree of micro-fracturing) and the association energy, which depends on the chemical characteristics of both HOCs and polymers.

2.3. Adsorption and partition in real plastics

As mentioned, the material in MPs typically exists as a heterogenous mixture of amorphous and crystalline states. Thus, sorption of HOCs to polymers is most likely an overlap between surface adsorption and internal partition. At high HOC concentrations in the water, saturation of surface binding sites will occur quickly, after which partition will dominate the sorption process, both kinetically and in terms of concentrations at equilibrium. The sorbed HOC mass per MP will behave according to Freundlich isotherms and specific chemical properties will have a smaller impact than the polymer's degree of crystallinity and the polar/nonpolar affinity between the HOC and the polymer. At low HOC concentrations adsorption will be responsible for a greater proportion of the total adsorbed concentration and thus, besides crystallinity, specific chemical affinities, particle size and degree of weathering

will be more important. This means that for some pollutant-polymer combinations where only linear isotherms have been obtained, an underlying adsorption effect could remain undetected (Figure 2).

Such understandings are not novel and have been proposed for other particulate sorbents. For instance, the sorption of PAHs and chlorinated benzenes (CBs) to natural soil particulates has been conceptualized as consisting of two separate domains: surface adsorption sites and internal partition space (Xia & Ball., 1999). Sorption of the nonpolar HOCs was successfully modelled for soil particulates using a hybrid Freundlich-Langmuir equation which accounted for adsorption at low HOC concentrations and partition at high concentrations. More sophisticated models were also proposed but retained the notion of overlapping adsorption and partition processes. Equation 3 is used to model simultaneous adsorption and partition on uptake of HOCs to soil solids (Xia & Ball, 1999). Notice that the first term is a Langmuir isotherm and the second is a linear Freundlich function:

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} + K_d C_e \quad \text{[Eq 3]}$$

Using this conceptual approach, the nonlinear effects of adsorption in sorption isotherms should become more visible with increasing crystallinity, but only at concentrations below the point at which all surface sites are occupied. Wang et al. (2015), for instance, found no correlation between K_d and the crystallinity of plastic lattices when studying the sorption of perfluorooctanesulfonate (PFOS) and perfluorooctansulfonamide (PFOSA) on polyethylene (PE), polystyrene (PS) and unplasticized polyvinylchloride (PVC). Sorption isotherms were linear for both HOCs on all polymers and the sorption capacity of the polymers at equilibrium was dependent entirely on the hydrophobicity of the polymers. However, the

concentrations employed (5-50 μg L^{-1}) in their experiments were orders of magnitude greater than those commonly reported in seawater (e.g. 1.5-5.7 ngL^{-1} Miyazke et al. 2014). At such high concentrations, all adsorption sites would be quickly occupied, and partitioning would overshadow any adsorption effects that may have occurred within the crystalline regions of PVC and PE. This underlines the necessity of performing laboratory studies in the same ranges of concentrations, and over relevant exposure times, as those in the environment to adequately represent sorption phenomena.

A recent review of HOC-MP interactions reported that very few studies were performed under field conditions and that even fewer related their findings to the concentrations found in the environment (O'Connor et al., 2016). This does not imply error in the findings, however, mechanistic understanding of sorption processes might be lost. Extrapolating sorption from higher concentrations to lower, more environmentally realistic, concentrations ignores important surface phenomena that occur at low concentration (Figure 2). In essence, modelling approaches that combine both sorption processes and take in consideration the parameters that affect both are likely the most accurate when dealing with realistic HOC-MP scenarios.

3. Considerations for laboratory to field extrapolations

The stated aim of many laboratory-based MP vector studies is to improve our understanding of this potential phenomenon in nature i.e. do aquatic organisms inadvertently accumulate HOCs by ingesting plastic debris? However, assessing environmental impact based on laboratory studies requires a number of extrapolations, which are relatively easy to justify when fundamental processes and conditions are similar between the laboratory set-up and the environment, but extrapolations become increasingly unreliable when there are

fundamental differences between the simulated and real-world scenarios. The considerations needed when attempting to extrapolate vector studies from laboratory to field have been previously discussed, primarily from the point of view of the organism's exposure to the HOC-MP complex (Khan et al., 2017: Mouneyrac et al., 2017). Such considerations include the suitability of test organism for use with particulate contaminants (MPs and nanoparticles (NPs)), principally with reference to feeding mode, physiologically relevant parameters of uptake route and site of action, and justifiable test choices such as exposure duration and test matrix. It is owing to such considerations that the current standardized toxicity test protocols (OECD, 2014) designed for solutes appear unsuitable for particulates (Khan et al., 2017).

Equally important and often overlooked in laboratory vector studies is to ensure that the interaction of HOCs with MPs is also environmentally realistic. In the following section we outline areas where extrapolation in this aspect of vector effect studies may be problematic and provide consideration on how studies can be designed to avoid extrapolation pitfalls. A conceptual schematic (Figure 3) indicates that moving away from the usual drawbacks of laboratory studies (i.e. the use of pristine MPs at unrealistic concentrations mixed with HOCs under unnatural conditions of short equilibrium time and hastened kinetics through mechanical agitation) to achieve greater environmental realism demands an increase in model complexity to characterize the HOC-MP interaction and account for simultaneous sorption processes at lower concentrations that can often be neglected.

3.1 Concentration

Extrapolating from high to low sorbate concentration poses a challenge in vector effect studies, since the sorption of HOCs at higher concentrations is governed by different mechanisms than at lower concentration (Figure 2). In keeping with studies on the sorption of

HOCs to soil and sediment particulates (Cornelissen et al. 2005) surface adsorption plays a more dominant role at the lower (environmentally realistic) concentration (below the saturation point of surface sites) as modeled by Langmuir isotherms (i.e. Figure 2B), whereas at higher chemical concentrations partition is more dominant and owing to the influx of chemicals into the MP structure. This implies that experiments performed at higher concentrations will expose organisms to HOCs mostly partitioned into amorphous areas of the MP, which might be less important than surface interactions at environmentally relevant conditions. The different kinetics at high and low concentrations further complicates direct extrapolations between such exposure scenarios.

3.2. Kinetics and equilibration time

Understanding whether HOC sorption to plastic particles has reached equilibrium is another important aspect. The path towards equilibrium is mainly dependent on two processes: intra-particle diffusion and aqueous boundary layer diffusion (ABLD). The rate of these processes thus determines the time it takes for the system to reach equilibrium. The sorption rates are related to the surface-area-to-volume ratio and the mobility of the HOCs in water and inside the plastic particles. In some scenarios this could lead to equilibrium half-life times of years or even centuries due to slow ABLD (Endo et al. 2013). Fundamental understandings of these processes, including ratio between crystalline/amorphous regions in the polymer and sorption kinetics for the relevant HOCs is therefore a paramount foundation for any extrapolation between elevated experimental sorption scenarios and slower environmental realistic scenarios.

In determining the sorptive properties of four polymers with seven HOCs, Hüffer and Hofman (2016) demonstrated that chemical properties (i.e. the structure or polymer

crystalline/amorphous character) as well as the hydrophobicity of the HOC were essential in determining the extent of sorption. Further key factors include both MP characteristics (particle size) and environmental conditions, such as temperature and salinity (Karapanagioti and Klontza, 2008; Zahn et al., 2016). Mechanical agitation (i.e. stirring) of the solution also plays a key role in sorption equilibrium, with the time to attain equilibrium being greater in static solution compared to more dynamic environment (Zahn et al., 2016). Accordingly, many vector studies employ agitation when adsorbing chemicals to MPs (e.g. Teuton et al., 2007; Bakir et al., 2014), but it is important to note that artificially hastening sorption kinetics may render such studies less environmentally realistic.

3.3. Specific HOC-plastic combinations

The majority of vector studies have limited themselves to certain type of MP (that is usually a microbead or sphere); polystyrene (PS) or polyethylene (PE) are commonly used with fewer studies employing PVC or other polymer types; and pristine with no degree of weathering or fouling combined with only one or a few notable PAHs (e.g. fluoranthene, pyrene, phenethrene) (e.g. Oliveria et al., 2013; Avio et al., 2015; Paul-Pont et al., 2016). Using such specific HOC-plastic combinations is justifiable when first investigating a new field or attempting to gain mechanistic insights as the reduction of variables under a controlled setting is advantageous. However, the restrictions of combinations invariably impact the validity of the extrapolation when trying to bridge the gap between field and laboratory scenarios.

A recent study by Wang and Wang (2018) described the sorption behavior of phenethrene on PE and nylon MP fibers derived from ropes and nets used in mariculture (Xiangshan Bay, China). Sorption, as described by Freundlich model for both fibers, was greater in the PE

295 fiber, suggesting the importance of functional groups on the plastic surface. Moreover,
296 smaller sized and rougher surfaces of the MPs tended to accelerate the sorption of
297 phenanthrene. This study is one of the first to illustrate that real-life MPs, in this case fibers,
298 adsorb HOCs in a situation that could potentially allow entry into the human food chain
299 (Wang et al., 2018).
300
301 Further complicating extrapolations is the fact that HOCs do not occur as single
302 compounds in the environment. Competition between different HOCs can have measurable
303 effects on all partition coefficients. For instance, Bakir et al. (2012) studied the competitive
304 sorption of phenanthrene and DDT on unplasticized PVC and polyethylene microbeads (200-
305 250 um) at environmentally relevant concentrations (0.8 - 3.1 μg L^{-1} for Phe and 0.8 - 1.7 μg
306 L^{-1} for DDT). They found that for uPVC the more hydrophobic DDT served as a sorption
307 antagonist for phenanthrene, resulting in lower K_d values (and nonlinear sorption isotherms)
308 for the PAH when DDT was added in higher concentrations.
309
310 **3.4. Weathering**
311 Weathering of MPs inevitably occurs over time within the aquatic environment and results
312 in the increase in the contact area that any given volume of plastic has with dissolved HOCs,
313 and ultimately the breakdown of MPs into even smaller fragments. In crystalline polymers,
314 specifically, nanovoids occur frequently due to such weathering. Water movement within
315 these nanovoids is null and the boundary layer volume is greater relative to the internal
316 volume affecting sorption kinetics. Such scenarios occur primarily from photo-weathering,
317 which causes bonds in the polymer matrix to break and formation of the nanovoids. This
318 results in increased diffusivity and sorption of HOCs (Hartman et al., 2017). Conversely,
319 weathering via photo-oxidation can reduce the hydrophobicity of the MPs by introducing

polar groups in the polymer structure (Fried et al., 2003) affecting the partition coefficient of HOCs, and likely lowering the total sorptive capacity of the MPs (Endo et al. 2005; Teuten et al. 2009).

Vector studies with weathered or aged MPs are yet to be fully researched, but recently Hüffer et al (2018) demonstrated that UV-aging (i.e. photo-oxidation) reduced the sorption capacity of HOC sorbates to PS MPs. Thus, when extrapolating from experiments with pristine particles to environmental realistic scenarios with weathered particles, it is important to understand how weathering under environmental conditions changes HOC-MPinteractions.

3.5. General considerations

Although polymers such as PP, PVC and PE are commonly used in sorption studies with a limited variety of HOC sorbates, methodologies can often differ in medium, equilibration time or the use and frequency of shaking (Zhan et al., 2016). Other considerations include that aging or the addition of complexing agents to solution can alter MP adsorption dynamics. The use of single chemicals in isolation lacks environmental realism as contaminants are more likely found in complex mixtures. It should also be noted that polymers are the major component of plastics but not the only one. The presence of additives and particularly plasticizers located in the amorphous regions will change their sorption properties sometimes significantly (Shashoua, 2008). With this in mind the general point we make, as illustrated by Figure 3, is that understanding HOC-MP interactions is vital. To extrapolate vector interactions to the real world requires recognition that study designs may require changing to accommodate these aforementioned considerations, which in turn may result in the use of more complex models and experimental procedures (as described in section 2.3).

4. Challenges and conclusions

The 'vector effect' is one aspect of MP research that remains open to debate (Koelmans et al., 2016). In order to fully understand whether MPs have a role in the transfer of HOCs to aquatic biota, it is vital that laboratory studies consistently consider the complexity of the HOC-MP interactions and make efforts towards environmental realism. This complexity is most evident and only relevant at the range of HOC concentrations that are found in the environment and therefore laboratory studies employing unrealistically high concentrations will overlook the intricacies of the sorption processes at lower concentrations, as only the dominant effect of phase partition is measured. Superimposing the results of characterizations performed at high concentrations and/or with unrealistic equilibration times on experiments conducted at the environmentally realistic natural conditions is inherently flawed.

Once accepting this, other aspects of the HOC-MP interaction must also be considered. In regard to the MP, the degree of crystallinity largely dictates the sorption process (at low concentrations) and therefore the appropriateness of the model used. The other factors outlined, including the use of pristine MPs (often in the form of almost pure polymers rather than formulated plastics) and inadequate equilibration times, all make for experiments that lack the desired level or realism. Instead of being avoided as experimental limitations, these challenges must be overcome. Thus within vector studies it is of paramount importance that the characterization of HOC-MP interactions is correctly and consistently modeled.

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561 **Figures Legends**

562

563 **Figure 1.** Schematic of the generalized interactions between hydrophobic organic
564 contaminants (HOCs) and microplastic (MP) particles. Crystalline regions are represented by
565 parallel, straight lines on the MP indicating tightly-packed polymers. The presence of
566 nanovoids within crystalline regions increase the surface area. In this region surface
567 adsorption dominates. Amorphous regions depicted as non-linear (wavy) lines indicate
568 loosely packed polymers where partition into the MP internal volume dominates. The outer
569 aqueous boundary layer (ABL) is the region surrounding the MP in which there is minimum
570 fluid movement and thus diffusive transport often limits the overall rate of
571 sorption/desorption processes. Double arrows indicate equilibrium between the environment
572 and different regions of the MP.

573

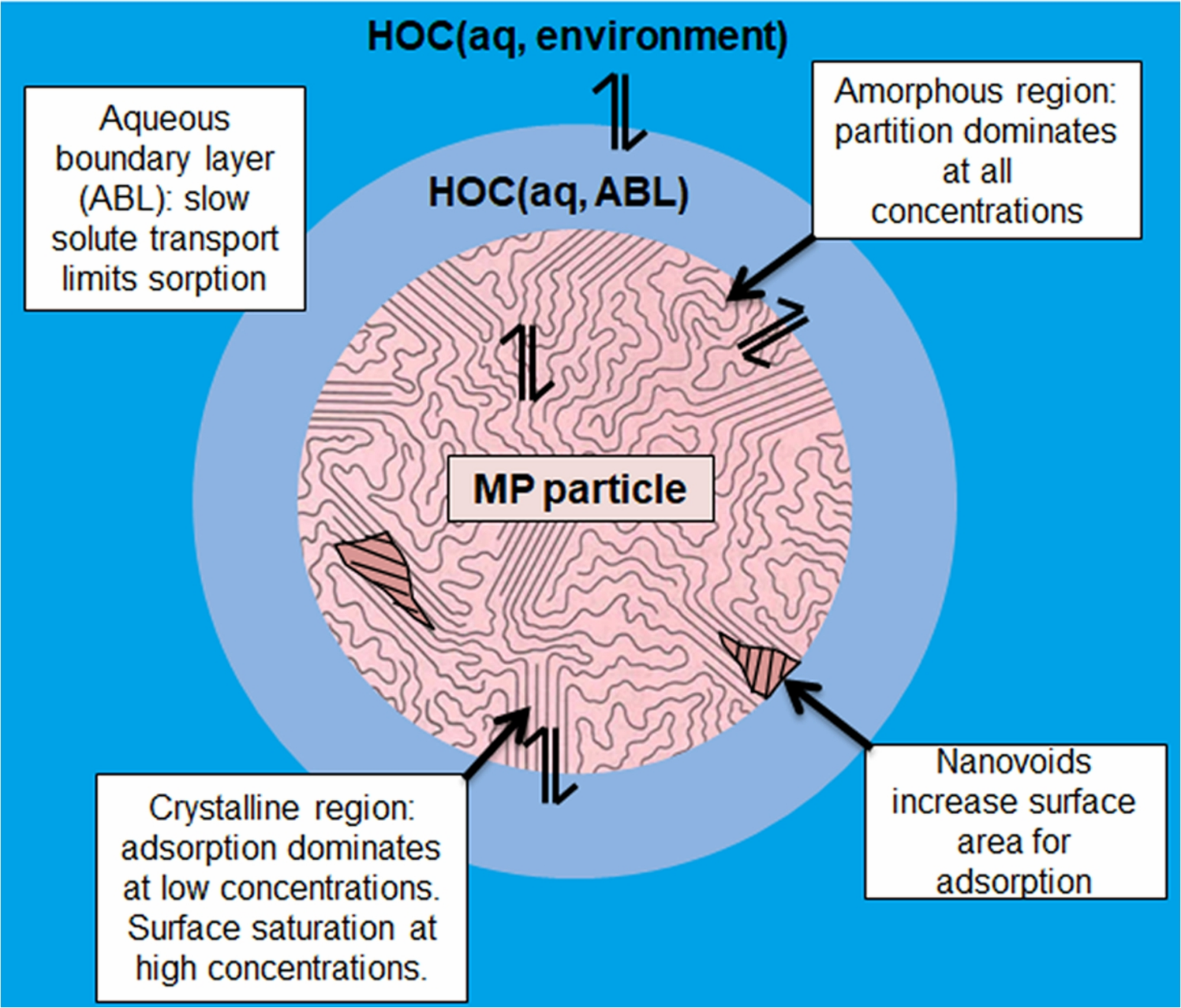
574 **Figure 2.** Hypothesized Freundlich (red dashed line), Langmuir (blue dashed line) and
575 Freundlich-Langmuir hybrid (black solid line) isotherms. Linear Freundlich plots
576 appropriately used to model HOC interactions with amorhpous MPs show similar isotherms
577 at high (A) and low (B) aqueous HOC concentrations. On the other hand, surface adsorption
578 onto glassy polymers modeled by Langmuir plots increases rapidly at low concentrations but
579 levels out at higher aqueous HOC concentrations. A mixed Freundlich-Langmuir model,
580 conceptually the more realistic approach to overall sorption in real MPs, is clearly
581 distinguishable from either of the other two at low concentrations, but is difficult to
582 differentiate from pure partition at higher concentrations. The figure illustrates the
583 importance of conducting HOC-MP sorption studies at the correct concentration range that
584 both mirrors the biological exposure of the vector study and allows the nature of the
585 interaction to be accurately determined.

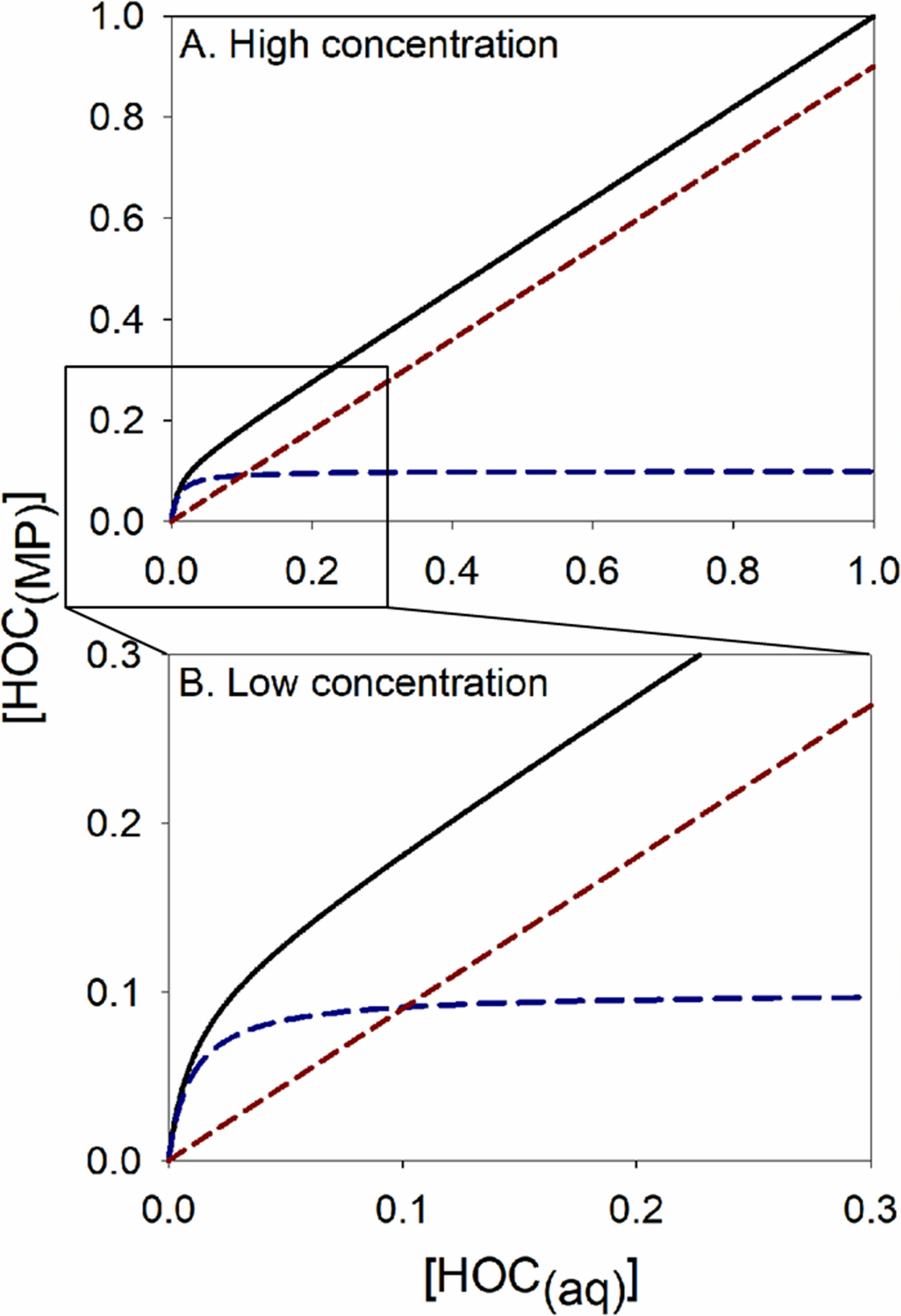
586

587 **Figure 3.** Conceptual schematic highlighting the factors needed to increase the
588 environmental realism of MP vector studies. The factors indicated, such as use of low
589 concentrations for HOC-MP characterizations, accounting for polymer structure, allowing
590 adequate equilibrium time with realistic kinetic considerations, using representative HOC-MP
591 combinations and non-pristine MPs all increase the environmental relevance of a study.
592 Conversely, studies conducted at higher HOC concentrations with pristine MPs where shorter
593 duration is allowed for equilibrium and that might employ stirring may be able to employ
594 simpler sorption models, but they are not easily extrapolated to the environment.
595

Highlights

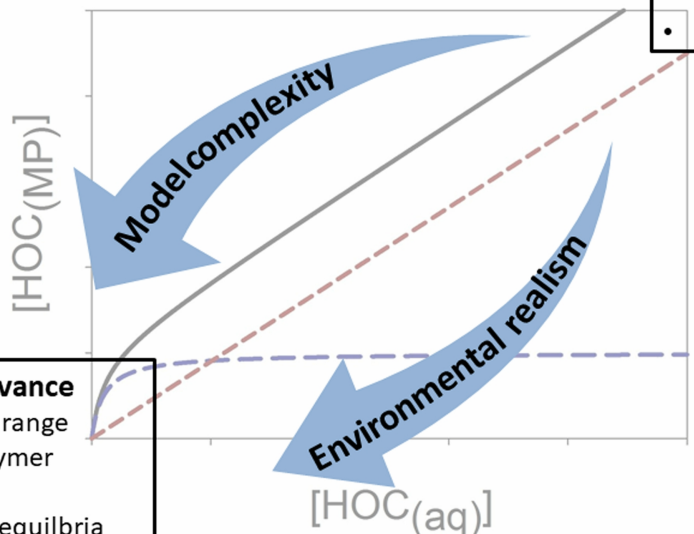
- Increased focus on understanding the microplastic (MP) vector effect.
- Characterisation of MP-HOC interactions may lack necessary considerations.
- We discuss the models needed when characterizing these interactions.
- We consider whether laboratory studies can be extrapolated to natural scenarios.


HOC(aq, environment)
Aqueous boundary layer (ABL): slow solute transport limits sorption
HOC(aq, ABL)
Amorphous region: partition dominates at all concentrations
MP particle
Crystalline region: adsorption dominates at low concentrations. Surface saturation at high concentrations.
Nanovoids increase surface area for adsorption


A. High concentration
B. Low concentration
[HOC(MP)]
[HOC(aq)]
1.0
0.8
0.6
0.4
0.2
0.0
0.3
0.1

Laboratory studies

- High concentration range
- Assumed polymer homogeneity
- Too short time to reach equilbium
- Hastened kinetics through agitation or stirring
- Pristine MPs



Environmental relevance

- Low concentration range
- Accounting for polymer structure
- Adequate time for equilbria
- Natural kinetics
- Weathered and fouled MPs